Journal of Non-Crystalline Solids 387 (2014) 6–15

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Evaluation of dielectric models for ceramic/polymer composites: Effect of filler size and concentration

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ARTICLE INFO

Article history:
Received 23 October 2013
Received in revised form 30 November 2013
Available online xxxx

Keywords:
Composites;
Dielectric constant;
$BaTiO_3$;
PZT;
PVDF

ABSTRACT

The main theoretical models for evaluation of the dielectric constant of ceramic/polymer composites are summarized and applied to PZT/poly(vinylidene fluoride) and $BaTiO_3$/poly(vinylidene fluoride) composites with varying filler concentration and size in order to evaluate the suitability of the models and the main interactions that are responsible for the composite dielectric behavior.

All models predict an increase in dielectric constant with increasing filler content. On the other hand, this increase is different for different models, showing the relative importance of the different interactions. Experimentally, the size of the inclusions plays an important role in determining the dielectric behavior of a composite, especially at the nanoscale. Effects occurring at the interface between the filler particles and the matrix become important as the relative surface area at the interface increases. Models not including fitting parameters do not properly represent the increase in dielectric constant with increasing filler content and none of them seem to properly represent the dielectric behavior of nanocomposites. In this way, the effects contemplated by the models – interactions between the particles, interactions with the field, depolarization factor or shape parameter – are not sufficient to account for the variations of the dielectric behavior related to the sizes of the particles.

1. Introduction

Piezoelectric ceramic/polymer composites are being increasingly used for multifunctional device, sensor and actuator applications [1–4]. The properties of each component of the composite, the processing conditions and the final microstructure strongly affect the final properties of the composite [5,6].

Ferroelectric ceramic/polymer composite for sensor and actuator applications typically consists of large dielectric constant ceramic particles embedded in a polymeric matrix, exhibiting good flexibility, low density, high dielectric constant, low dielectric losses and, in many cases, large piezoelectric coefficients that result from the combination of the properties of both components [4,7]. The interfacial interaction between ceramic particles and polymer influences/determines the final thermal, mechanical, dielectric and piezoelectric properties of the composite materials [8–10]. For example, the absence of interfacial adhesion between ceramic particles and polymeric matrix results in a decrease in dielectric constant and piezoelectric coefficients of the composite materials [11,12].

Electroactive polymer more intensively studied is poly(vinylidene fluoride), PVDF, due to its outstanding piezoelectric properties, when compared with other polymers. It is semi-crystalline and can exhibit four crystalline phases, α, β, γ and δ, depending on processing conditions [13,14].

The most studied and used polymorphs of PVDF are the α- and β-phases. α-phase is obtained when the polymer is cooled from melt, while β-phase, which exhibits the largest piezo-, pyro- and ferroelectric properties [15,16], can be obtained by mechanical stretching of α-phase films at controlled temperatures between 70 and 100 °C [17], directly from solution at temperatures below 70 °C [18] and by the incorporation of specific fillers such as clays [19], zirconia [20], carbon nanotubes [21], ferrite nanoparticles [22], ceramic particles ($BaTiO_3$) [23] and silver nanoparticles [24], among others, within the polymer matrix.

The piezoelectric ceramic particles most used in ceramic/polymer composites are lead zirconate titanate, $Pb(Zr_xTi_{1-x})O_3$ or PZT and barium titanate, $BaTiO_3$, both crystallizing in perovskite structure [25]. Both materials have high dielectric and piezoelectric coefficients at room temperature: $\varepsilon = 811$, $d_{33} = 246$ pC/N at 1 Hz for PZT and $\varepsilon = 1200$ ($\Phi = 10$ nm); $\varepsilon = 3417$ ($\Phi = 500$ nm) and $d_{33} = 100$ pC/N for $BaTiO_3$ [26–29].

The phase diagram of PZT exhibits a morphotropic phase boundary (MPB) that divides the ferroelectric region in two parts: a rhombohedral phase region rich in Zr and a tetragonal phase region rich in Ti. It is located at Zr/Ti = 52/48 [30,31]. With that concentration the material shows the largest elecroactive properties, including the larger dielectric and piezoelectric response.

The phase diagram of $BaTiO_3$ is not as complex as that of PZT, but, depending on the temperature, it exhibits five crystalline phases, hexagonal, cubic, tetragonal, orthorhombic, monoclinic and rhombohedral [32].

Dielectric constant of a composite is determinant for applications and for understanding the nature of the interactions between the

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http://dx.doi.org/10.1016/j.jnoncrysol.2013.12.005

constituents of the composite. There are many theoretical studies on dielectric constant of composites in order to describe its dependence on the volume fraction of the filler particles, the dielectric constant of polymer and filler and the possible interaction between both constituents [33–38]. To properly determine the accuracy of the different theoretical models is particularly important for their use in the prediction of the static dielectric constant and therefore the design of ceramic-polymer composites for specific applications.

Simple models, such as Maxwell–Garnett and Rayleigh, have been used to describe the experimentally obtained dielectric behavior of composites as a function of the ceramic filler content [39–43]. Nevertheless, more complex models have been developed to include, for example, shape parameters [44], as it has been observed that the most simple models underestimate the experimental growth of the dielectric constant with filler content due to the unconsidered interactions and the effect of ceramic particles aggregates in the polymer matrix [39]. Despite the models being still often used in the literature, their equations do not fit the experimental data precisely. Thus, it was concluded that the effective dielectric permittivity also depends on shape and size of the filler particles [42], which is not considered by most simple models. The role of the interface between the polymer and the ceramic phases has also often been ignored [45].

In the literature, different theoretical models are typically applied to different ceramic/polymer composite systems, with the models introducing different physical fundaments for describing the interactions between the ceramic and the polymer.

In this work, a systematic comparison and critical analysis of the models is performed in order to evaluate the main interactions and parameters considered by each one of them. It will be shown which of the models is more appropriate in taking account filler concentration and filler size (micro and nanoscale), by applying the different models to a ceramic–polymer composite system. This evaluation is performed by fitting the models to the same collection of PZT/PVDF and $BaTiO_3$/PVDF composites experimental data.

In PZT/PVDF composites, the effect of PZT concentration up to 40% volume is analyzed for three average sizes of the ceramic particles, 0.84, 1.68 and 2.35 μm. In the case of $BaTiO_3$/PVDF composites, the filler size different in orders of magnitude: 10 and 500 nm.

The analyzed theoretical models are classified into three groups, which are summarized in Table 1.

Group 1 calculates the dielectric constant of a composite assuming dielectric spheres dispersed in a continuous matrix. They include Rayleigh [37], Maxwell–Garnett [36], Lichtenecker [47], Sillars [47] and Furukawa [33]. No interactions between its constituents are taken into account.

Group 2 contemplates interactions between filler with neighboring particles and with applied electric field. These models include Bruggeman [37], Maxwell–Garnett [36], Böttcher [49], Kerner [37], Looyenga [50], Paletto [37], Tinga [51], Bergman [46], Jayasundere [48] and Poon [52].

Group 3 models introduce depolarization factor, which takes into account the shape and orientation of the inclusions. The respective functions are Wiener [38], van Beek [56], Tinga [51], Bergman [46], Yamada [34], Yonezawa [37] and Rother [38].

2. Dielectric models

In the equations presented below (Eqs. (1) to (27)), v is the volume fraction and ε is the dielectric constant, the subscripts 1 and 2 represent the matrix and filler, respectively.

Table 1
Summary of the theoretical models considered in the present work. In the equations below, v is the volume fraction and ε is the dielectric constant, the subscripts 1 and 2 represent the matrix and filler, respectively.

Group	Model	Equation	Ref.	Plotted in figure(s)
1	Rayleigh	$\varepsilon=\frac{2\varepsilon_1+\varepsilon_2-2v_2(\varepsilon_1-\varepsilon_2)}{2\varepsilon_1+\varepsilon_2+v_2(\varepsilon_1-\varepsilon_2)}\varepsilon_1$	[37]	1 and 3
	Maxwell–Garnett	$\varepsilon=\varepsilon_1\left[1+\frac{3v_2\gamma}{1-v_2\gamma}\right],\gamma=\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_2+2\varepsilon_1}$	[36,46]	Same result as Eq. (1)
	Lichtenecker	$\ln(\varepsilon)=v_1\ln(\varepsilon_1)+v_2\ln(\varepsilon_2)$	[47]	1 and 3
	Sillars	$\varepsilon=\varepsilon_1\left[1+\frac{3v_2(\varepsilon_2-\varepsilon_1)}{2\varepsilon_1+\varepsilon_2}\right]$	[47]	1 and 3
	Furukawa	$\varepsilon=\frac{1+2v_2}{1-v_2}\varepsilon_1$	[33]	1 and 3
2	Bruggeman	$v_1\frac{\varepsilon_1-\varepsilon}{\varepsilon_1+(d-1)\varepsilon}+v_2\frac{\varepsilon_2-\varepsilon}{\varepsilon_2+(d-1)\varepsilon}=0$	[37,46]	2 and 4
	Maxwell–Garnett	$\varepsilon=\varepsilon_1\left[1+\frac{3v_2\gamma}{1-v_2\gamma-\frac{2}{3}v_2\gamma\ln\left(\frac{8+\gamma}{8-2\gamma}\right)}\right]$	[36]	2 and 4
	Böttcher	$\frac{3\varepsilon}{\varepsilon_1+2\varepsilon}v_1+\frac{3\varepsilon}{\varepsilon_2+2\varepsilon}v_2=1$	[49]	Same plot as Eq. (7) for $d=3$
	Kerner	$\varepsilon=\frac{\varepsilon_1(1-v_2)+v_2\varepsilon_2\xi}{(1-v_2)+v_2\xi},\quad\xi=\frac{3\varepsilon_1}{2\varepsilon_1+\varepsilon_2}$	[37,48]	2 and 4
	Looyenga	$(\varepsilon)^{1/3}=(\varepsilon_1)^{1/3}v_1+(\varepsilon_2)^{1/3}v_2$	[50]	2 and 4
	Paletto	$\varepsilon=v_2\frac{(1-v_2)\varepsilon_1\gamma^2+v_2\varepsilon_2}{[1+(1-v_2)(\gamma-1)]^2}+(1-v_2)\frac{(1-v_2)\varepsilon_1+v_2\varepsilon_2\xi^2}{[(1-v_2)+v_2\xi]^2}$ $\gamma=\frac{3\varepsilon_2}{\varepsilon_1+2\varepsilon_2},\xi=\frac{3\varepsilon_1}{2\varepsilon_1+\varepsilon_2}$	[37]	2 and 4
	Tinga	$\frac{\varepsilon-\varepsilon_1}{\varepsilon_1}=v_2\frac{3(\varepsilon_2-\varepsilon_1)}{2\varepsilon_1+\varepsilon_2-v_2(\varepsilon_2-\varepsilon_1)}$	[51]	Same plot as Eq. (7) for $d=3$
	Bergman	$\left(\frac{1}{d\varepsilon_1}+\frac{1}{\varepsilon-\varepsilon_1}\right)^{-1}=v_2\left(\frac{1}{d\varepsilon_1}+\frac{1}{\varepsilon_2-\varepsilon_1}\right)^{-1}$	[46]	Same plot as Eq. (7) for $d=3$
	Jayasundere	$\varepsilon=\frac{\varepsilon_1v_1+\varepsilon_2\gamma}{v_1+\gamma}$ $\gamma=\frac{3\varepsilon_1v_2}{2\varepsilon_1+\varepsilon_2}\left(1+3v_2\frac{\varepsilon_2-\varepsilon_1}{2\varepsilon_1+\varepsilon_2}\right)$	[48]	2 and 4
	Poon	$\varepsilon=\varepsilon_1+\frac{v_2(\varepsilon_2-\varepsilon_1)}{v_2+(1-v_2)\frac{\varepsilon_2+2\varepsilon_1-v_2(\varepsilon_2-\varepsilon_1)}{3\varepsilon_1}}$	[52]	2 and 4
3	Wiener	$\frac{\varepsilon-1}{\varepsilon+n'}=\frac{v_2(\varepsilon_2-\varepsilon_1)}{\varepsilon_2+n'}+\frac{(1-v_2)(\varepsilon_1-1)}{\varepsilon_1+n'}$	[38]	No valid solution
	Van Beek	$\varepsilon=\varepsilon_1\frac{\varepsilon_1+[n(1-v_2)+v_2](\varepsilon_2-\varepsilon_1)}{\varepsilon_1+n(1-v_2)(\varepsilon_2-\varepsilon_1)}$	[56]	Same plot as Eq. (25)
	Tinga	$\frac{\varepsilon-\varepsilon_1}{\varepsilon_1}=v_2\frac{\varepsilon_2-\varepsilon_1}{\varepsilon_1+n_2(\varepsilon_2-\varepsilon_1)-n_1v_2(\varepsilon_2-\varepsilon_1)}$	[51]	5
	Bergman	$\varepsilon=\varepsilon_1+v_2\varepsilon_2\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_2+n(\varepsilon_1-\varepsilon_2)}$	[46]	5
	Yamada	$\varepsilon=\varepsilon_1\left[1+\frac{n'v_2(\varepsilon_2-\varepsilon_1)}{n'\varepsilon_1+(\varepsilon_2-\varepsilon_1)(1-v_2)}\right]$	[34]	5
	Yonezawa	$\frac{\varepsilon-1}{\varepsilon+n'}=\sum v_i\frac{\varepsilon_i-1}{\varepsilon_i+n'}$	[37]	Same plot as Eq. (25)
	Rother	$\ln(\varepsilon)=\ln(\varepsilon_1)+v_2(1-n')\ln\left(\frac{\varepsilon_2}{\varepsilon_1}\right)$	[38]	5 a)